

PB-215 017

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PEAK INTENSITIES OF HYDROCARBONS

A. P. Altshuller, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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ABSTRACT

The pressure-broadening effects of one atmosphere of air or of carbon dioxide on various infrared bands of hydrocarbons have been measured and compared with the intensity data obtained without pressure-broadening. Measurements have been made on the following hydrocarbons at partial pressures between 0.5 and 20 millimeters and at the following wavelengths: ethylene, 10.52 microns; acetylene, 3.1, 7.4 and 13.7 microns; propylene, 10.95 microns; butene-1, 10.85 microns; trans-2-butene, 10.375 microns; and benzene, 9.50 microns. The variation of optical absorbance at several of the infrared absorption maxima of ethylene and acetylene have been investigated using varying partial pressures of air or carbon dioxide at fixed partial pressures of the two hydrocarbons.

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INTRODUCTION

The quantitative infrared analysis of gas mixtures resulting from combustion processes or atmospheric pollution usually is done at atmospheric pressures. The effects of the partial pressures of nonabsorbing gases on the absorption band of a particular component being analyzed may be of considerable significance.

The appreciable effects of varying the pressure of various non-absorbing gases in the gas cell on the optical absorbance at the absorption band maxima of given polar or nonpolar gaseous species have been known for many years. In comparatively recent years there have been several relevant publications (1-6). These investigations point out a number of empirical generalities that may be used to advantage in analytical applications. However, some gaps exist in the information as to the magnitude of the pressure-broadening effects on two- through four-carbon hydrocarbons. Also it is not clear whether or not ~~any~~ pressure-broadening effects might be observable for some absorption bands of five-carbon and larger molecules in the gaseous state. Furthermore, few of the available data have been obtained with the partial pressures of the absorbing gas below 20 millimeters. Finally, the magnitude of the differential effects of substituting a higher molecular weight gas such as carbon dioxide for lower molecular weight nonabsorbing gases does not appear to have been investigated in detail. It appeared that the substitution of 10 to 15 percent carbon dioxide for

oxygen in combustion mixtures might have a small but significant pressure-broadening effect. The present investigation was initiated to gain some further information on these problems.

EXPERIMENTAL

The hydrocarbons used were Matheson instrument or C.P. grade or Phillips 99 + mole percent gases and reagent grade benzene. These materials were used as received.

The infrared data were obtained with a Beckman IR-4 infrared spectrophotometer using sodium chloride optics and standard slit-widths. Peak absorbancies were obtained either with the wavelength drive stopped at the wavelength of the peak maxima or with a scanning speed of 0.02 microns per minute.

The absorption cell used was a Perkin-Elmer multiple-pass cell fixed at 1.25 meters optical path length. The windows on the cell were silver chloride plane-convex lenses.

In the preliminary measurements which included the measurements of the broadening of several of the ethylene and acetylene peaks at various partial pressures of air and carbon dioxide, the cell was evacuated down to about 0.2 millimeter once and then filled with the hydrocarbon gas. The mercury manometer was so situated that the gas volume in one arm of the manometer was included in the total volume measured. Since the gas volume in the arm changed with pressure, the total volume available also changed. Since the cell itself has a 6.3-liter volume, this error actually was fairly small.

During the later work in which the pressure-broadening was measured with the addition of one atmosphere of air or carbon dioxide, the absorption cell was filled by a different and probably more desirable procedure than that used in the preliminary measurements. In these later determinations,

the cell was pumped down and filled with the hydrocarbon under investigation several times before finally adjusting the partial pressure of the gas. This procedure should insure the absence of air or carbon dioxide in the cell or inlet lines. The hydrocarbon gas was pumped out until the partial pressure was about that desired as judged by the absorbance readings, the vacuum pump was cut out of the system, and the pressure read on a McLeod gauge. The portion of the system containing the McLeod gauge and U-type mercury manometer was then cut off. Finally, the inlet line was disconnected. The bottom of the valve leading to the cell was flushed with carbon dioxide prior to pressure broadening with this gas.

The benzene was vaporized into the infrared cell from a small liquid reservoir containing the benzene until an appropriate pressure was reached.

RESULTS

Pressure-broadening by both air and carbon dioxide increases the intensities of the maxima of the carbon-hydrogen bending vibration of ethylene at 10.52 microns and the P branch of the parallel band of acetylene at 7.63 microns from 300 to 500 percent as shown in Table I. The results indicate that the intensity of the carbon-hydrogen bending vibration of propylene at 10.95 microns is increased by 20 to 35 percent by one atmosphere of air or carbon dioxide. The intensity of the maximum of the corresponding carbon-hydrogen bending vibration of trans-butene-2 at 10.38 microns is very slightly increased by air or carbon dioxide (see Table I). The data given show that the broader peak at 10.85 microns of butene-1 is increased in intensity by about the same amount as the sharper band of trans-butene-2.

The absorption maxima of ethylene, propylene, butene-1, trans-butene-2 are all increased in intensity very slightly by one atmosphere of carbon dioxide compared with one atmosphere of air, as may be seen in Table II.

However, the maximum of the 7.63-micron band of acetylene is increased in intensity appreciably more by one atmosphere of carbon dioxide compared to one atmosphere of air.

It might not be expected that absorption bands of as large a molecule as benzene would undergo pressure-broadening. Nevertheless, the results listed in Table I indicate that the rather sharp vibrational band of benzene at 9.50 microns increases in intensity by 12 to 14 percent at partial pressures of 2.3, 5.0 and 10.0 millimeters of benzene, using one atmosphere of air or carbon dioxide to cause pressure-broadening. No significant difference was observed in the pressure-broadening of the 9.50-micron band of benzene by carbon dioxide compared to air.

Small partial pressures of air or carbon dioxide cause marked increases in the intensities of the ethylene band at 10.5 microns and acetylene band at 13.7 microns, as may be seen in Figures 1-3. The intensity of the 10.5-micron band of ethylene is about doubled when 20 millimeters of air are added to one millimeter of ethylene. The 13.7-micron band of acetylene is almost tripled in intensity by 20 millimeters of carbon dioxide or air.

The variation in the absorbancies of the maxima of the 3.1-, 7.4-, and 13.7-micron bands of acetylene is given in Figure 3 as a function of the partial pressure of carbon dioxide. The 13.7 micron band is much more sensitive to pressure-broadening by carbon dioxide than is the carbon-hydrogen stretching vibration at 3.1 microns, which in turn is more sensitive to pressure-broadening than is the 7.4 micron band.

As can be seen from Figures 1 and 3, even the hydrocarbon absorption bands which are most sensitive to pressure-broadening are not significantly affected by appreciable variations in pressure in the range near 760 millimeters. Variations in atmospheric pressure by 20 or 30 millimeters from

the pressure used in the calibration analyses should have no significant effect on the accuracy of the determination.

DISCUSSION

The present results provide additional evidence as to the appreciable pressure-broadening experienced by at least some of the prominent infrared absorption bands of two- and three-carbon hydrocarbon molecules. The data presented have indicated that the bending vibrations of butene-1 and trans-butene-2 are only slightly pressure-broadened. No pressure-broadening has been reported previously for the 8.47-micron band of isobutene or the 6.26-micron band of butadiene-1,3 (2). However, these investigators (2) did find slight pressure-broadening of the 11.0 micron of butadiene-1,3. Similarly, Nielsen and his coworkers (2) reported very little, if any, effect of total pressure on the other absorption bands of the four-carbon hydrocarbons which they investigated.

Pressure-broadening has not been reported previously for any of the infrared absorption bands of benzene (2,6). However, the data given in Table I at three partial pressures of benzene varying over a fourfold range of concentration, and using both air and carbon dioxide as pressure-broadening gases, clearly indicates that the 9.50-micron band is so affected. While deviations from ideal gas behavior in the gas mixture compared to the benzene alone would have a slight effect in the same direction, the magnitude of such an effect would be too small. No artifact occurs to the present investigators which would explain the results. Consequently, at present, we must accept the results as providing evidence for a real pressure-broadening effect for as large a molecule as benzene.

The results obtained for the 3.1-, 7.4- and 13.7-micron bands of acetylene indicate the wide variations in pressure-broadening existing among

different bands of the same molecule. Caution should be used in drawing conclusions about the effects of pressure-broadening on other infrared bands of a molecule from experimental results on any given band of that molecule.

The present investigation does indicate that carbon dioxide often has a greater pressure-broadening effect on the bands of light hydrocarbon than does air. However, the difference is not enough to make 10 or 15 percent of carbon dioxide in a combustion mixture of significance in comparison with an equivalent amount of oxygen. Consequently, calibration mixtures of hydrocarbons made up in air should be adequate in reproducing conditions in combustion mixtures for the purposes of infrared analysis.

LITERATURE CITED

1. P.C. Cross, and F. Daniels, J. Chem. Phys. 2, 6(1934).
2. J.R. Nielsen, V. Thornton, and E.B. Dale, Rev. Mod. Phys. 16, 307 (1944).
3. N.D. Coggeshall, and E.L. Saier, J. Applied Phys. 17, 450 (1946).
4. W.D. Seyfried, and S.H. Hastings, Anal. Chem. 12, 278 (1947).
5. J.C. Perlend, and J. Archinard, J. Phys. Radium 15, 835 (1954).
6. R.A. Friedel, and J.A. Queiser, Anal. Chem. 22, 1362 (1957).

TABLE I

PRESSURE-BROADENING DATA ON VARIOUS INFRARED BANDS OF HYDROCARBONS
USING ON¹ ATMOSPHERE OF THE BROADENING GAS

Compd.	max.	Conc. range, mm.	Broadening gas	% increase in intensity
ethylene	10.52	0.63, 1.00	air	470-500
			CO ₂	480-550
acetylene	7.63	5-20	air	310-440
			CO ₂	410-500
propylene	10.25	0.45-1.5	air	20-30
			CO ₂	20-37
butene-1	10.85	1.0, 3.0	air	1
			CO ₂	4
trans-butene-2	10.37	0.70, 1.92	air	1
			CO ₂	4
benzene	7.50	2.3-10.0	air	12-14
			CO ₂	13-14

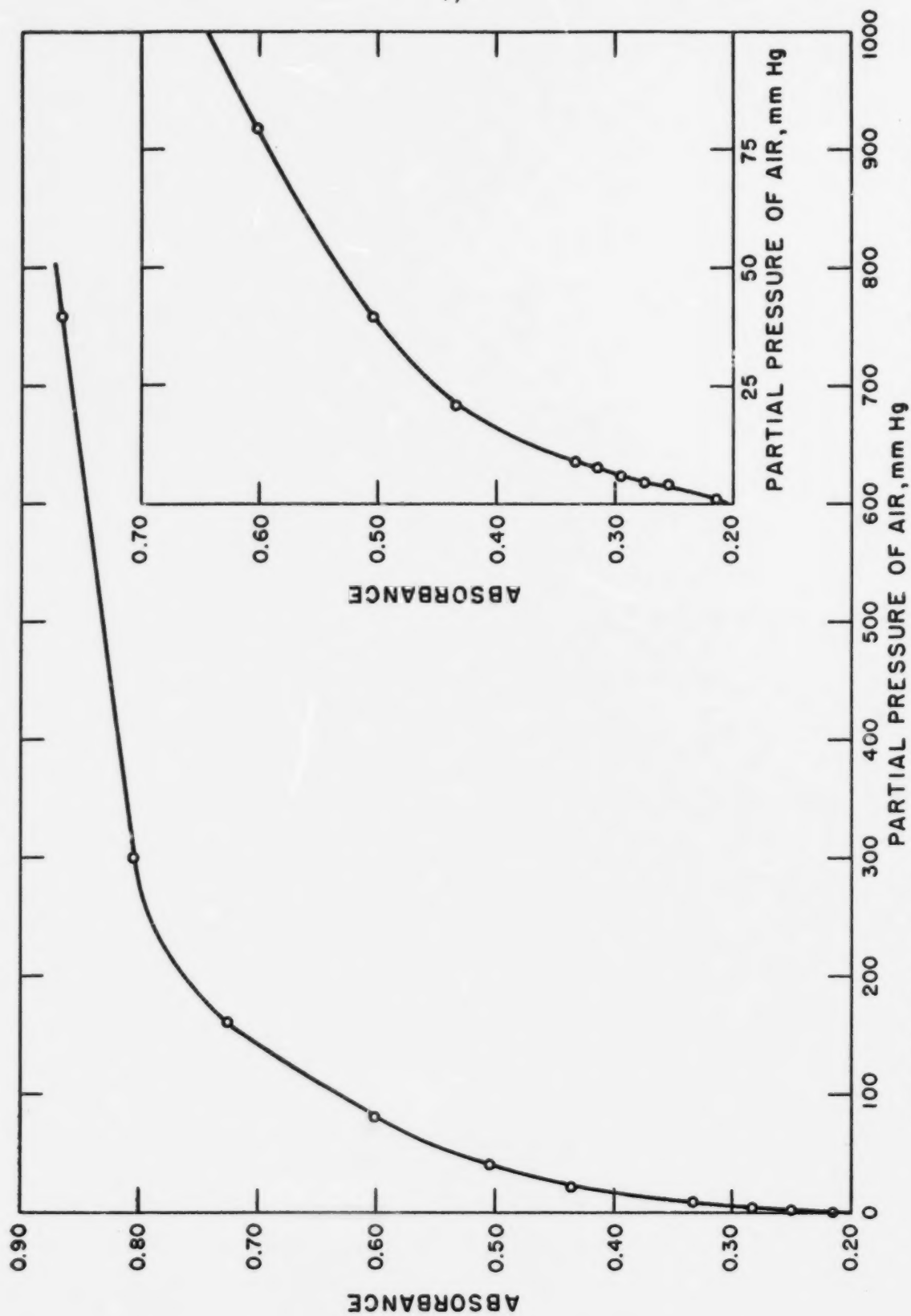
TABLE II

COMPARISON OF PRESSURE-BROADENING EFFECTS OF ONE ATMOSPHERE OF AIR OR CO₂ ON ETHYLENE, ACETYLENE AND PROPYLENE

Compound	λ_{max}	Partial pressure, mm.	Broadening gas	Absorbance
ethylene	10.52	0.63	air	0.506 ± 0.024
			CO ₂	0.518 ± 0.043
		1.03	air	0.856 ± 0.028
			CO ₂	0.907 ± 0.019
acetylene	7.63	5.0	air	0.222 ± 0.003
			CO ₂	0.257 ± 0.005
acetylene	7.63	10.0	air	0.361 ± 0.001
			CO ₂	0.432 ± 0.003
propylene	10.95	0.97	air	0.472 ± 0.006
			CO ₂	0.484 ± 0.002
trans-2-butene	10.37	1.92	air	0.718 ± 0.012
			CO ₂	0.733 ± 0.010

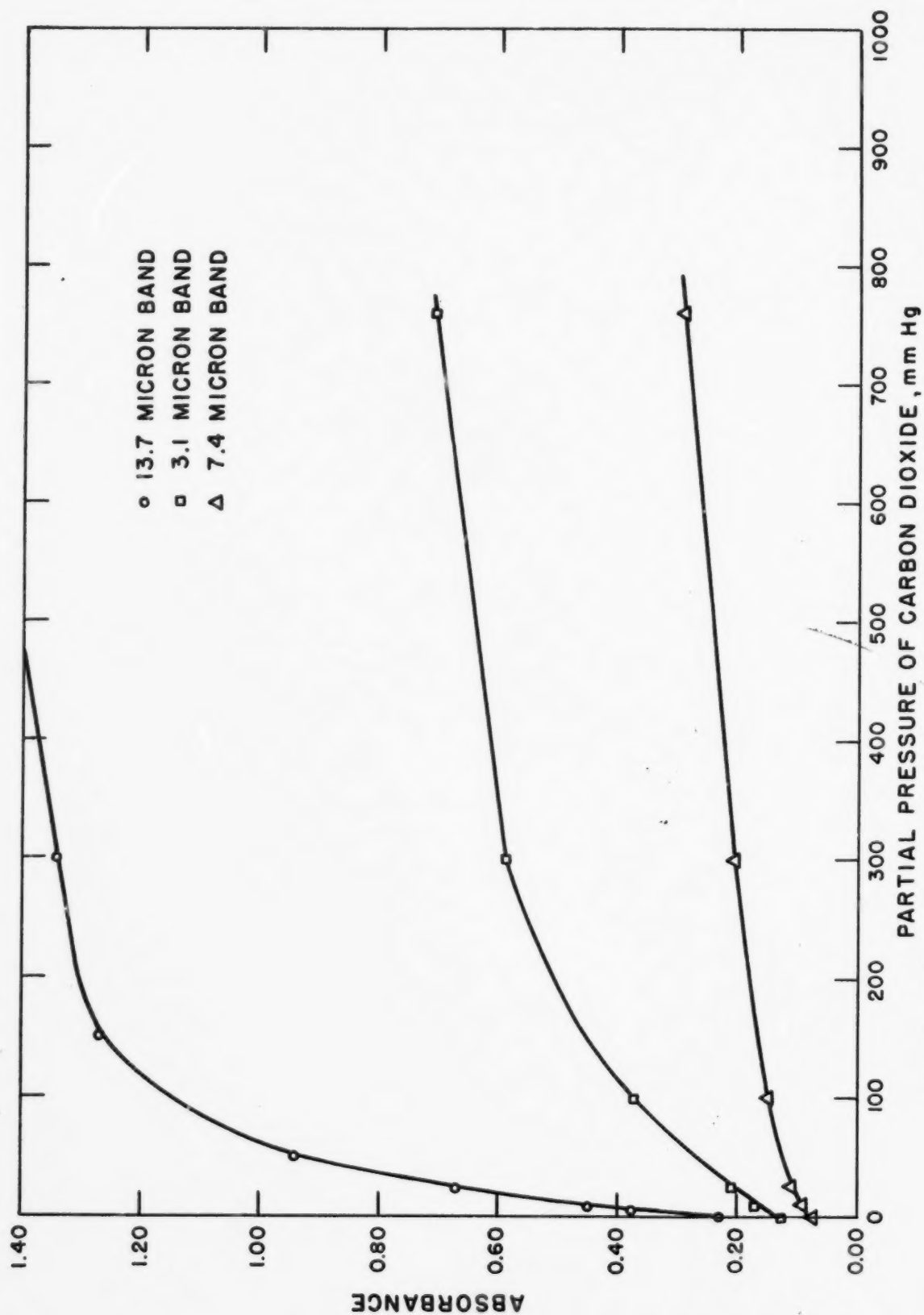
LIST OF FIGURES

- Figure 1. Pressure-broadening of 10.5 micron band of ethylene (1.15 mm ethylene) by air.
- Figure 2. Pressure-broadening of several acetylene bands (0.7 mm acetylene) by carbon dioxide.
- Figure 3. Pressure-broadening of 13.7 micron band of acetylene (0.84 mm acetylene) by air.



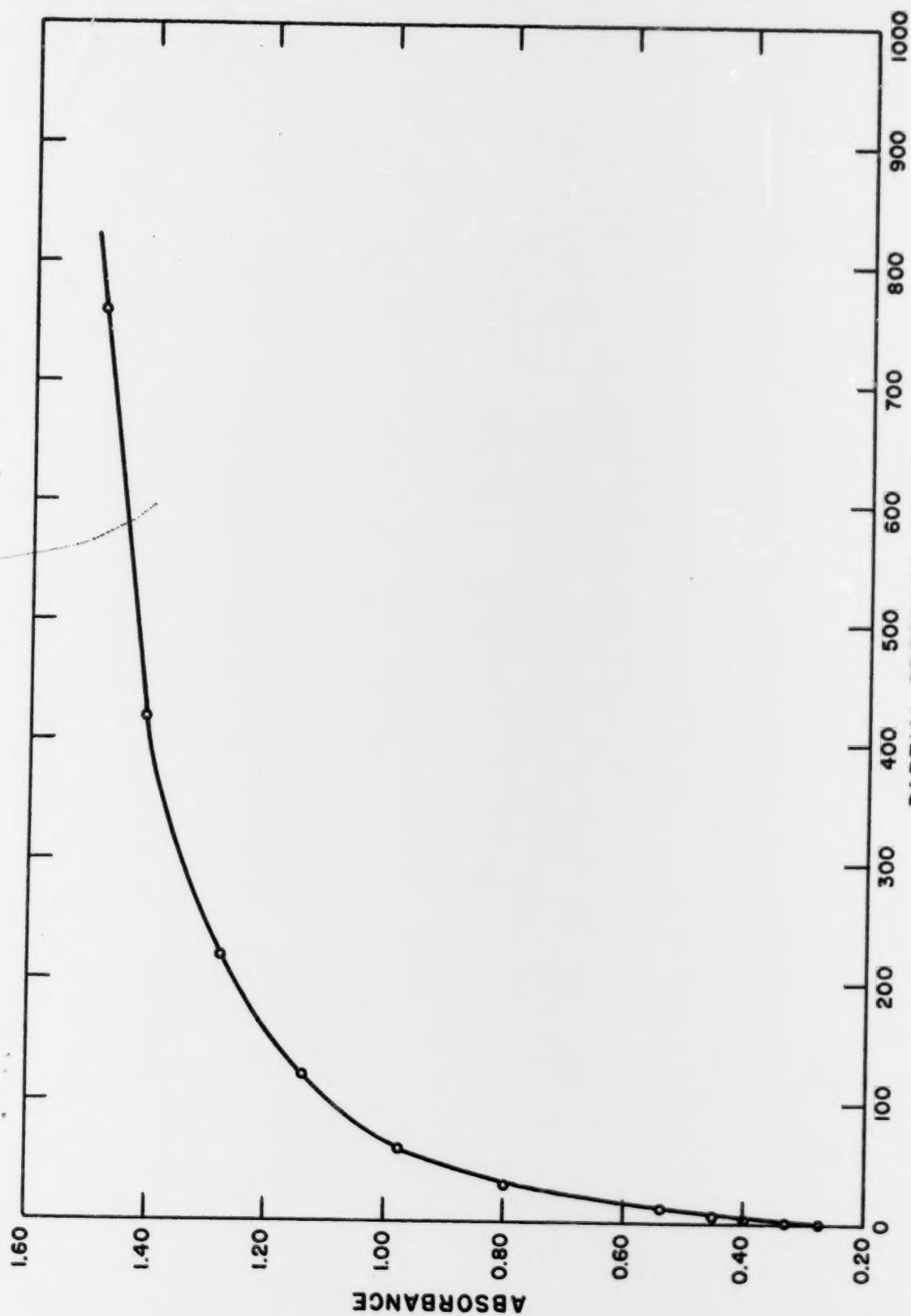
PRESSURE - BROADENING OF 10.5 MICRON BAND OF ETHYLENE
(1.15 mm ETHYLENE) BY AIR

FIGURE I



PRESSURE - BROADENING OF SEVERAL ACETYLENE BANDS
(0.7 mm ACETYLENE) BY CARBON DIOXIDE

FIGURE 2



PRESSURE - BROADENING OF 13.7 MICRON BAND OF ACETYLENE
(0.84 mm ACETYLENE) BY AIR

FIGURE 3